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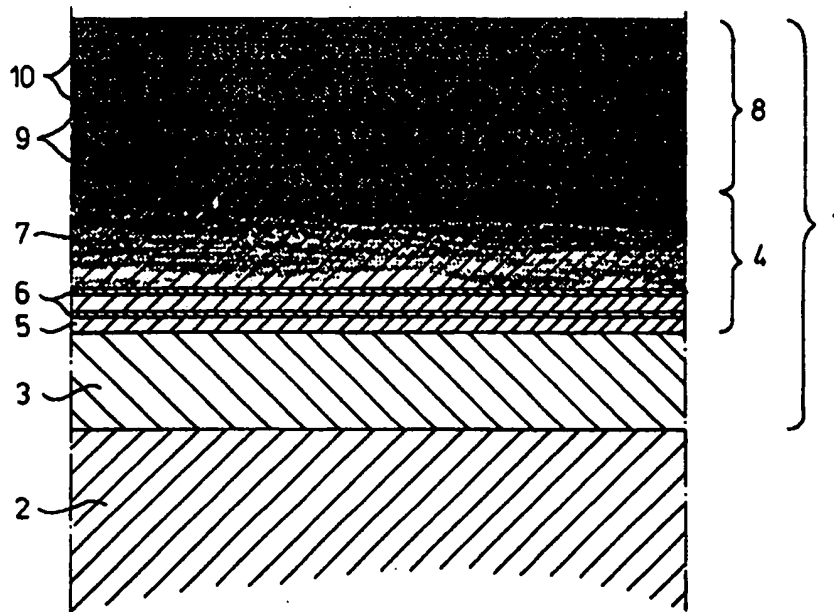
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(54) Title: COATED ROLLING ELEMENT BEARING



(57) Abstract

A rolling element bearing, comprises an inner ring, an outer ring and rolling elements which are in rolling contact with the raceways of the inner ring and the outer ring. The rolling elements and/or the raceway (2) of at least one of the rings is coated with a metal-mixed diamond-like carbon layer (8).

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WO 99/14512

PCT/NL98/00533

1

Coated rolling element bearing

The invention is related to the field of rolling element bearings. Rolling element bearings are applied in various environments. As long as lubrication is guaranteed, their normal design life can generally be obtained without problems.

Under poor or marginal lubrication conditions however, the behaviour of rolling element bearings is less favourable. In such cases, it may prove to be impossible to form a lubricant film, resulting in direct metal-to-metal contact of the rolling elements and the rings, and thus leading to adhesive wear, such as fretting, and premature failure.

Also, rolling element bearings which are exposed to periods of vibratory or oscillatory motions while under static load without rotation of the bearing often show a phenomenon known as "False-Brinelling", which again can limit bearing life.

As a consequence of these phenomena, the service life under poor lubrication conditions is greatly impaired. Attempts have been made to alleviate this problem by applying hard coatings onto the bearing components, e.g. comprising carbide and nitride coatings (e.g. TiN, TiC, CrN), as well as solid lubricants such as molybdenum di-sulphide.

None of these attempts however has yielded a significant improvement. Although nitride and carbide coatings have high hardness levels and do offer a good abrasive wear resistance and high hardness, their friction coefficients are high. These high friction coefficients in combination with high hardness leads to abrasive wear of the counterface, i.e. of a ring or rolling element.

Furthermore, the high adhesion of TiC, TiN and CrN coatings is only attained with relatively high coating temperatures of the order of 400 °C. Such coatings are widely used for cutting tools where the substrate material is made from highly alloyed high speed steel which retains hardness at temperatures of 500 to 540 °C, due to the phenomenon of secondary hardening. Such coating temperatures would result in excessive softening and dimensional changes with the lower alloyed steels that are commonly used in rolling element bearings.

According to US-A-5108813, normal diamond-like carbon coatings can be applied in sliding bearings. A diamond-like carbon coating is defined as a layer of amorphous hydrogenated carbon consisting of both sp³ and sp² hybridised carbon

WO 99/14512

PCT/NL98/00533

2

bonds. While in sliding bearings the adhesion of a diamond-like carbon coating to the substrate is sufficient, in rolling element bearings such coatings flake off as a result of the much higher contact stresses in a rolling element bearing.

The object of the invention is therefore to provide a rolling element bearing
5 which has an increased service life under conditions where lubrication is poor or absent. This object is achieved in that the rolling elements and/or the raceway of at least one of the rings is coated with a metal mixed diamond-like carbon coating.

The metal mixed diamond-like carbon coating according to the invention offers both low friction and high wear resistance, even under the high contact stress levels
10 encountered in rolling element bearings (such stresses can be up to 3 or 4 GPa). The diamond-like carbon coating according to the invention, mixed with carbide forming metal atoms is capable of supporting these high contact stress levels without flaking within itself or from the substrate, when the coating structure is optimized to give high adhesion.

15 Thus, the coating in question is suitable for application for rolling element bearings operating under dry conditions or where lubrication is poor or even absent.

According to the preferred embodiment, the metal mixed diamond-like-carbon coating is formed on a metallic interlayer of Cr, W, Mo, or Al, which is pre-deposited onto the substrate surface. There should be a gradual transition of the
20 metallic interlayer into the metal mixed coating. The diamond-like carbon coating, applied to the metallic interlayer, also contains one or more metallic carbide forming elements such as W, Mo or Ti.

The metal mixed diamond-like-carbon part of the coating may be composed of alternating parallel layers of predominantly diamond-like-carbon, but containing some
25 metal carbide, and predominantly metal carbide, but containing some diamond-like-carbon, each of the order of 1 to 50 nanometre thickness.

Alternatively, the metal carbide can be in the form of clusters interspersed throughout a layer of diamond-like-carbon. Such layers consists of a matrix of predominantly diamond-like carbon with a dispersion of particles of metal carbide.
30 Said particles can have a clustered morphology giving regions (clusters) of metal carbide up to 100 nm in extent. The clusters may be composed of carbides of one or more metals.

WO 99/14512

PCT/NL98/00533

3

The thickness of the metal mixed diamond-like-carbon coating can be up to 10 μm . The multi-layer structure of the coating gives rise to reduced residual stresses in the coating and therefore enhanced adhesion compared to conventional single layer diamond-like-carbon coatings with or without a metallic interlayer.

- 5 A further important feature of the coating is the possibility to decrease the metallic carbide forming element content towards the surface during the coating process, thereby increasing the diamond like character of the outer layers of the coating. This still results in high adhesion to the substrate but at the same time also allows a significant increase in the surface hardness as the outer layer of the coating
- 10 is now closer to pure diamond like carbon. In this case, the low friction and increased hardness gives benefits of increased wear resistance, whilst retaining high adhesion necessary for rolling bearing applications.

- Also, there can be a gradual increase in graphite content towards the coating surface. This has the benefit of further reducing the friction coefficient. Of course,
- 15 both a reduction of the metallic carbide forming element, and an increase in the graphite content towards the coating surface can be achieved.

The metal mixed diamond like carbon coating may also contain metallic Ni or possibly Fe as a means of reducing cost of the carbide forming element source material.

- 20 Furthermore the metal-mixed diamond-like-carbon coating can be applied at a coating temperature of $< 240\text{ }^{\circ}\text{C}$, with the high adhesion levels necessary for rolling element bearings. In this respect temperature sensitive low alloy bearing steels in the hardened and tempered condition can be coated in such a way that microstructural or phase changes of the substrate material do not occur, with the result that there are no
- 25 permanent irreversible size changes of the coated bearing components. This allows assembly of rings and/or rolling elements with standard components and avoids the need of matching in order to obtain the desired bearing precision and internal clearance.

- In addition the low coating temperature ensures that the substrate hardness and
- 30 fatigue properties of temperature sensitive low alloy bearing steels are not impaired and that standard static and dynamic capacity ratings for the bearing still apply. Nevertheless, the coating can also be applied to high alloy steels, such as martensitic stainless steels and high speed steels.

WO 99/14512

PCT/NL98/00533

4

The invention will be explained further with reference to the examples shown in the figures.

Figure 1 shows a first embodiment of the invention.

Figure 2 shows a second embodiment of the invention.

5 Figure 1 shows a cross-section to the outer layers of the rolling element or raceway of a ring of a rolling element bearing. The full outer part has been indicated in its entirety by reference No. 1, and has been applied to a substrate 2, e.g. bearing steel.

 Said full outer part 1 comprises an intermediate metallic interlayer 3, which
10 has been applied directly onto the substrate 2, a transition zone 4 which follows the intermediate metallic interlayer 3, and a metal-mixed diamond-like carbon coating 8. The transition zone 4 comprises an area wherein a multi-layer transition is obtained, with alternating metal-carbide layers 5 and metallic layers 6. Subsequently a smooth transition area 7 is obtained, into the multi-layer structure 8. The transition area 7
15 provides a smooth transition from metal-carbide to a mixture of metal-carbide and diamond-like carbon. Said multi-layer structure 8 comprises alternating metal carbide layers 9 and diamond-like carbon layers 10.

 Figure 2 shows a cross-section to an alternative embodiment, also of the outer layers of a rolling element as the raceway of a ring of a rolling element bearing.

20 The full coating 11 comprises a matrix 12 of predominantly diamond-like carbon, with a dispersion of metal carbide particles 13. Such particles or clusters 13 of metal carbide may have a maximum dimension of 100 nm.

 The substrate 2, interlayer 3 and transition zone 4 are similar to the corresponding ones in the embodiment of figure 1.

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WO 99/14512

PCT/NL98/00533

5

Claims

1. Rolling element bearing, comprising an inner ring, an outer ring and rolling elements which are in rolling contact with the raceways of the inner ring and the
5 outer ring, characterized in that the rolling elements and/or the raceway of at least one of the rings is coated with a metal-mixed diamond-like carbon (1), coating (8-10, 11-13).

2. Rolling element bearing according to claim 1, and comprising ancillary
10 components such as a cage, seals, shields and/or a guide ring which are in contact with the rings, rolling elements and/or another of said components, wherein at least one of said ancillary components is coated with a metal-mixed diamond-like-carbon coating (8-10, 11-13)).

15 3. Rolling element bearing according to claim 1 or 2, wherein the thickness of the metal-mixed diamond-like-carbon coating (8-10, 11-13) is up to 10 μm .

4. Rolling element bearing according to claim 1, 2 or 3, wherein the metal-mixed diamond-like-carbon coating (8-10, 11-13) is coated onto a metallic
20 intermediate layer (3).

5. Rolling element bearing according to claim 4, wherein the metal-mixed diamond-like carbon coating (8-10, 11-13) is coated onto a metallic intermediate layer (3) of Cr, W, Mo or Al.
25

6. Rolling element bearing according to claim 4 or 5, wherein between the metal-mixed diamond-like-carbon coating (8-10, 11-13) and the intermediate metallic layer (3), there is a transition zone (4).

30 7. Rolling element bearing according to any of the preceding claims, wherein the metal-containing diamond-like-carbon coating (8-10, 11-13) has been applied by coating at a temperature of $< 240\text{ }^{\circ}\text{C}$.

WO 99/14512

PCT/NL98/00533

6

8. Rolling element bearing according to claims 1, 2 and 3, where there is a gradual reduction of the metallic carbide forming element (preferably W, Mo or Ti) content towards the coating surface such that the outer regions of the coating become more diamond like carbon in nature.

5

9. Rolling element bearing according to any of the preceding claims, wherein there is a gradual increase in graphite content towards the coating surface.

10. Rolling element bearing according to any of the preceding claims, wherein the metal-mixed diamond-like-carbon-coating (8-10, 11-13) contains Ni.

11. Rolling element bearing according to any of the preceding claims, wherein the metal-mixed-diamond-like coating (8) comprises alternating layers (10) of predominantly diamond-like-carbon, and layers (9) of predominantly metal carbide (9).

12. Rolling element bearing according to any of the preceding claims, wherein the metal-mixed-diamond-like coating (8) comprises alternating layers (10) of predominantly diamond-like-carbon, but containing some metal carbide, and layers (9) of predominantly metal carbide (9), but containing some diamond-like-carbon.

13. Rolling element bearing according to any of claims 1-10, wherein metal is in the form of clusters (13) interspersed throughout a matrix (12) of diamond-like-carbon.

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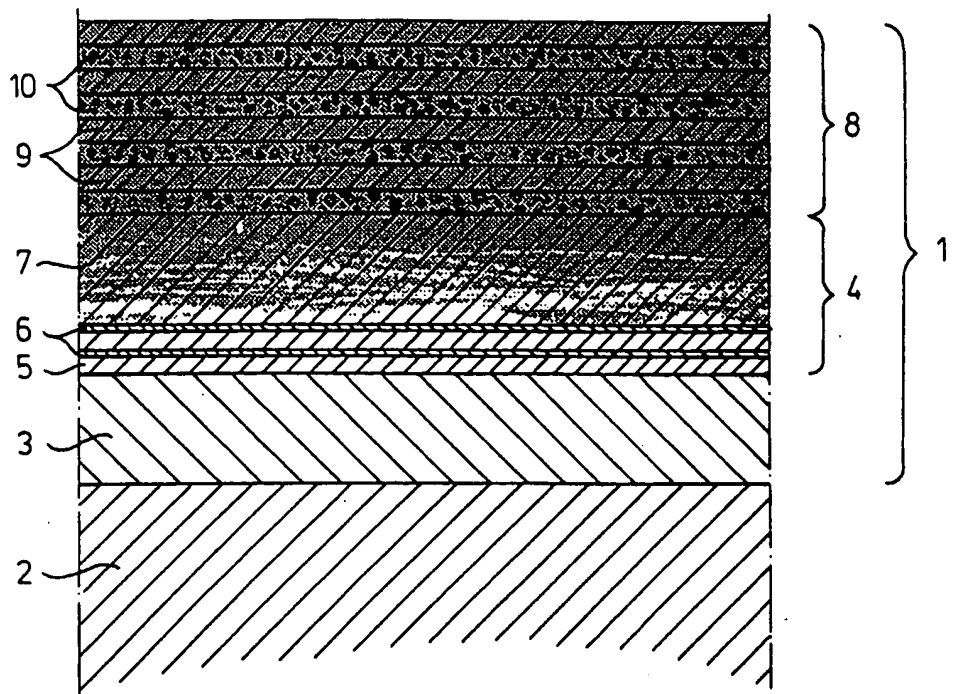
14. Rolling element bearing according to claim 13, wherein the maximum extent of the clusters is 100 nm.

WO 99/14512

PCT/NL98/00533

1/2

fig-1

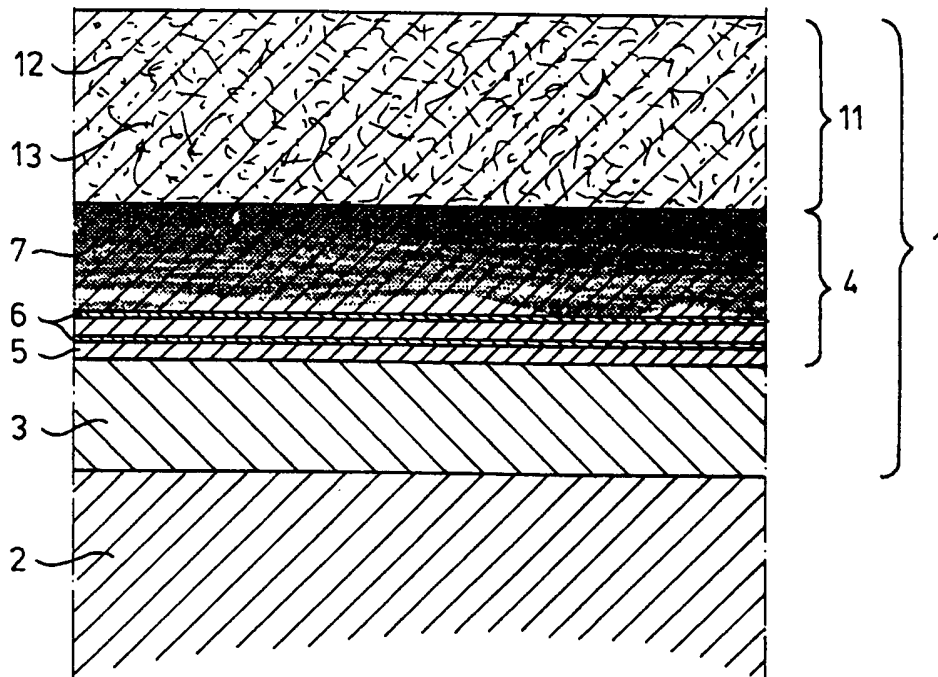


WO 99/14512

PCT/NL98/00533

2/2

fig-2



INTERNATIONAL SEARCH REPORT

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	PATENT ABSTRACTS OF JAPAN vol. 95, no. 3, 28 April 1995 & JP 06 341445 A (SHOJIRO MIYAKE), 13 December 1994 see abstract ---	1,2
X	US 5 593 234 A (LISTON) 14 January 1997 see column 10, line 18 see column 10, line 34 - line 40 ---	1,3,4,7, 11
A	WO 95 12693 A (UTC) 11 May 1995 see page 3, line 20 - line 23 see page 9, line 18 - line 21 ---	1-5,7
A	US 5 631 761 A (LEE) 20 May 1997 see column 1, line 53 - line 58 see column 2, line 37 - line 60 ---	1,3,4
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Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 540 636 A (MAC IVER) 10 September 1985 see the whole document ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 17, no. 617 (C-1129), 15 November 1993 & JP 05 186870 A (SEIKO), 27 July 1993 see abstract ---	1,6,8
A	EP 0 438 775 A (GENERAL ELECTRIC) 31 July 1991 see claim 5 ---	1,2
A	US 4 960 643 A (LEMELSON) 2 October 1990 see the whole document ---	1
A	US 5 108 813 A (NODA) 28 April 1992 cited in the application see the whole document -----	1

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5593234	A	14-01-1997	JP 9133138 A	20-05-1997
WO 9512693	A	11-05-1995	US 5482602 A	09-01-1996
			AU 8086094 A	23-05-1995
US 5631761	A	20-05-1997	NONE	
US 4540636	A	10-09-1985	DE 3447447 A	04-07-1985
			JP 60159168 A	20-08-1985
			US 4554208 A	19-11-1985
			US 4618505 A	21-10-1986
EP 438775	A	31-07-1991	US 4962519 A	09-10-1990
US 4960643	A	02-10-1990	US 5456406 A	10-10-1995
			US 4974498 A	04-12-1990
			US 5096352 A	17-03-1992
			US 5040501 A	20-08-1991
			US 5067826 A	26-11-1991
			US 5255929 A	26-10-1993
			US 5132587 A	21-07-1992
			US 5288556 A	22-02-1994
			US 5284394 A	08-02-1994
			US 5332348 A	26-07-1994
			US 5360227 A	01-11-1994
US 5108813	A	28-04-1992	JP 2620976 B	18-06-1997
			JP 3040984 A	21-02-1991

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